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(54) **Blends of polyethersulfones with aromatic polyimides, polyamides or polyamide-imides and gas separation membranes made therefrom.**

(57) The present invention provides a three-component blend of (i) an aromatic polyethersulfone, (ii) an aromatic polyimide, and (iii) an alkyl-substituted aromatic polyimide, polyamide or polyamide-imide or mixtures thereof. The invention also provides for gas separation membranes with superior gas transport properties made from two-and-three-component blends of polyethersulfone with aromatic polyimides to provide a gas separation membrane with superior productivity and good selectivity.

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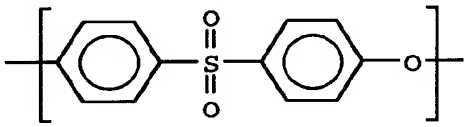
FIELD OF THE INVENTION

The present invention relates generally to three-component blends of aromatic polyethersulfones, an aromatic polyimide and an alkyl-substituted aromatic polyimide, polyamide or polyamide-imide. The invention also relates to gas separation membranes cast from a two-component or three-component polymer blend of aromatic polyethersulfones with an aromatic polyimide and/or an alkyl-substituted aromatic polyimide, polyamide or polyamide-imide. The precise gas transport properties of the membrane may be adjusted based on the blending of the specific polymer components.

BACKGROUND OF THE INVENTION

It is well known to modify polymer properties through blending to obtain inexpensive materials with improved characteristics. Polymer blends are broadly classified into homogeneous (miscible) and heterogeneous (immiscible) blends. Homogeneous blends are relatively rare; however, a homogeneous blend of an aromatic polyethersulfone and an aromatic polyimide has been described in the art. In particular, "Thermal and Rheological Properties of Miscible Polyethersulfone/Polyimide Blends" by K. Liang, J. Grebowicz, E. Valles, F. E. Karasz and W. J. MacKnight, published in the Journal of Polymer Science: Part B: Polymer Physics, Vol. 30, pp. 465-476 (1992) describes a miscible blend of an aromatic polyethersulfone (commercial name VICTREX®) and an aromatic polyimide (commercial name MATRIMID® 5218) over the entire blend composition range, particularly blends containing less than 10% of the aromatic polyimide.

Aromatic polyethersulfones are not, however, miscible with other aromatic polyimides, polyamides or polyamide-imides. This immiscibility, along with excellent high-temperature properties and high softening temperatures, have made blends of aromatic polyethersulfones and aromatic polyimides, polyamides or polyamide-imides very difficult to fabricate into many products. The fabrication of films, coatings, and other structures from blends of aromatic polyethersulfones and aromatic polyimides, polyamides or polyamideimides generally requires elaborate processes. Particularly, it is known that the aromatic polyethersulfone having the following repeating formula:



is not miscible with certain alkyl substituted aromatic polyimides, polyamides or polyamide-imides.

It is also generally known that gas separation membranes may be cast from polymers. The separation of gas components by polymer membranes is thought to depend on chemical affinities, kinetics and structural characteristics; it being known that rubbery polymers are generally characterized by high diffusion and relatively low selectivity while glassy polymers are generally characterized by lower diffusion and higher selectivities.

Polymer blending has traditionally been thought to be either problematic or of no benefit in the membrane field, primarily because different polymers are generally not miscible with one another. Those few polymers which are thought to be miscible offer no blending advantage in the membrane field because of various reasons, including difficulty in blending, poor mechanical properties, limited range of gas transport properties, and complex relationships between blend composition and gas transport properties.

U.S. Patent No. 5,055,116 describes a blend of certain aromatic polyimides, in which the blending of the polymer components is adjusted to achieve certain permeability and selectivity of a polymer membrane. The final properties of a new polymer membrane may be predicted so that a membrane with those desired final properties can then be manufactured.

SUMMARY OF THE INVENTION

The present invention provides for a three-component blend of (i) an aromatic polyethersulfone, (ii) an aromatic polyimide, and (iii) an alkyl substituted aromatic polyimide, polyamide or polyamide-imide or mixtures thereof. The miscible blend offers unique fabrication opportunities not available to immiscible blends. Particularly, the present invention also provides for gas separation membranes made from (i) a two-component blend of an aromatic polyethersulfone and an aromatic polyimide, and (ii) a three-component blend of (a) an aromatic polyethersulfone, (b) an aromatic polyimide and (c) certain alkyl-substituted polyimides, polyamides or poly-

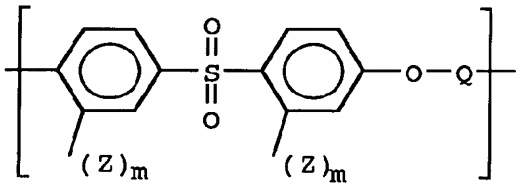
amide-imides or mixtures thereof. The gas permeability and selectivity of these membranes is superior. The inventive membranes prepared from the blends of this invention are extremely useful in separation processes involving, for example, H_2, N_2, CH_4, CO, CO_2, He, and O_2, by virtue of the high permeability and selectivity exhibited by membranes made from the polymer blends.

DETAILED DESCRIPTION OF THE INVENTION

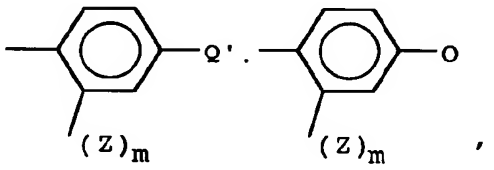
The present invention provides for a three-component blend. The blend comprises (i) an aromatic polyethersulfone, (ii) an aromatic polyimide, and (iii) certain alkyl-substituted aromatic polyimides, polyamides or polyamide-imides or mixtures thereof.

The blend miscibility of the polymers may be confirmed by the presence of single composition dependent glass transition temperature lying between those of the constituent blend components. Differential Scanning Calorimetry was used to measure glass transition temperature.

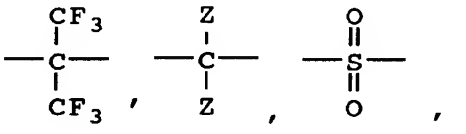
The aromatic polyethersulfone used in the three-component blend has the following repeating unit:

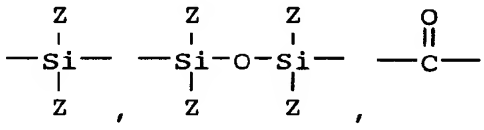


where Q is preferably nothing or has the following formula:



where t is 0 or 1, preferably 0 and Q' is

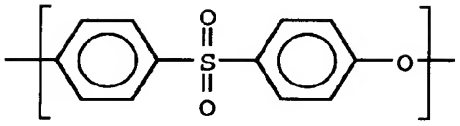




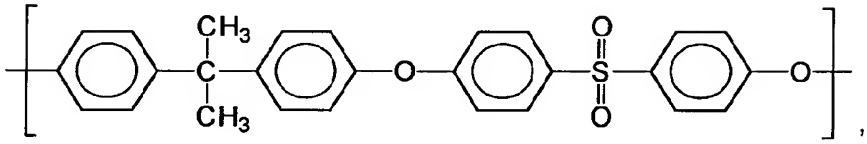
or mixtures thereof.

Z in all cases is independently -H, alkyl groups having 1-6 carbon atoms, aromatic groups having 6-12 carbon atoms, or halogen groups such as -F, -Cl, -Br or -I. Z is preferably -H. m is an integer from 0 to 4, preferably 0.

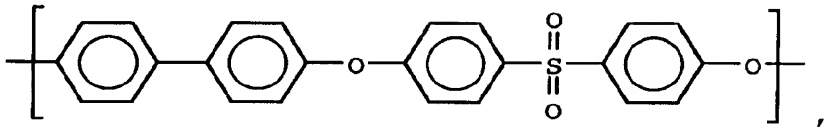
Preferred polyethersulfones which are commercially available have the following repeating chemical structures:



available from ICI Americas Corp. as VICTREX®;

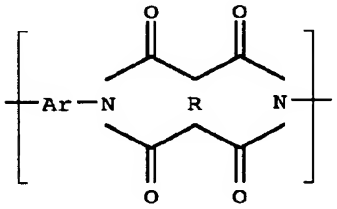


available from Amoco Corp. as UDEL®; and

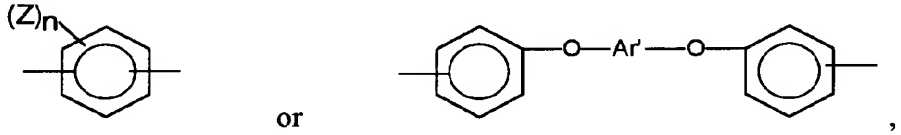


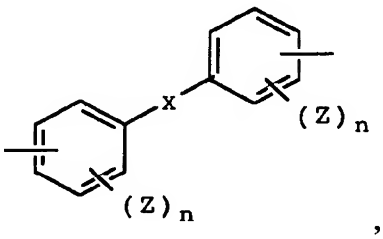
available from Amoco Corp. as RYDEL®.

Alkyl-substituted aromatic polyimides useful in the present invention contain at least one of the following unit:



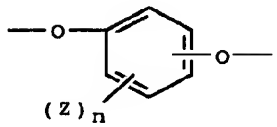
where -Ar- is an aromatic diamine moiety having the following formula:



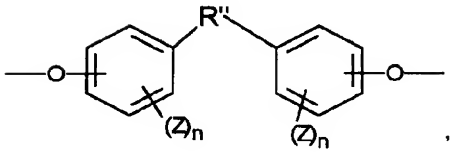


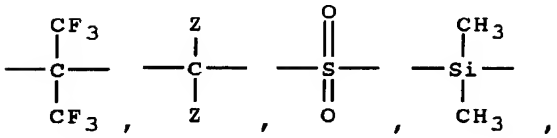
where -Ar'- is

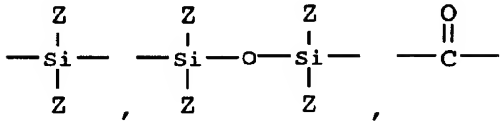
where X = nothing or R', preferably nothing.



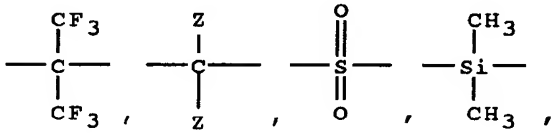
-R'- is

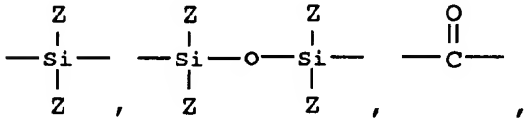




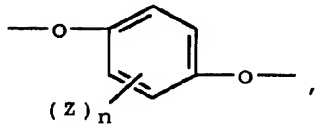


or mixtures thereof, where Z is defined above. Preferably, Z is a tertiary butyl group and n = 1. R" is

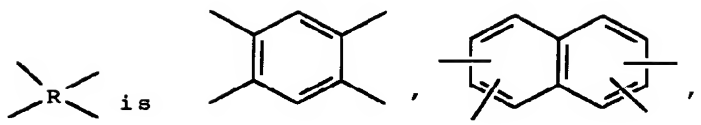


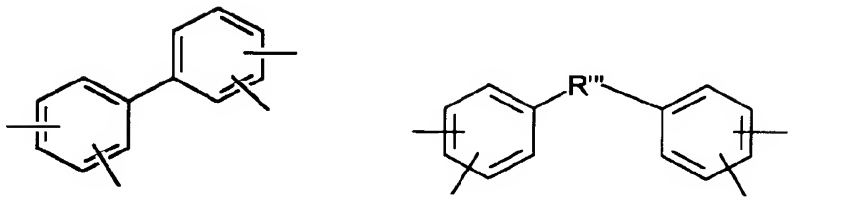


or

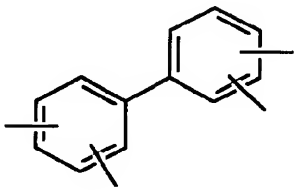


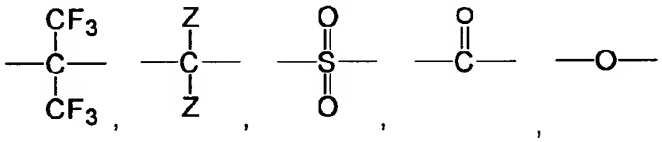
, or mixtures thereof.





or mixtures thereof, preferably





R''' is
R' described above, or mixtures thereof.

In general, the polyimides of this invention have a weight average molecular weight within the preferred range of from about 23,000 up to about 400,000 and more preferably from about 50,000 up to about 280,000.

In the preferred process for preparing the polyimides of this invention, approximately equimolar quantities of a dianhydride and the diamine are reacted by well-established procedures known in the art. In general, this process involves the polycondensation of the diamine and the dianhydride followed by the dehydration of the resulting polyamic acid to form a polyimide.

Preferably, the diamine is first dissolved in a polymerization solvent medium and the dianhydride is then gradually added portionwise under continuous agitation. After the addition of all of the monomer, the concentration of the reactants should be such that a solution concentration within the range of about 10 to about 30% by weight (preferably about 20% by weight) is achieved. Additional solvent may be added if necessary to achieve this level.

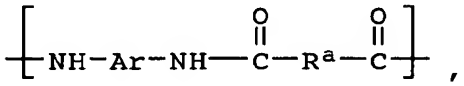
The solvents which may be used in the polymerization process are organic solvents, preferably polar aprotic, whose functional groups do not react with either the dianhydride or diamine reactant to any appreciable extent, and in which either the dianhydride or diamine, preferably both, and the polymer are soluble. Examples of suitable solvents include N,N-dimethylformamide or N,N-dimethylacetamide; dimethylsulfoxide, N-methylpyrrolidone; gamma-butyrolactone; pyridine; diglyme; and like materials as well as mixtures of such solvents.

Polymerization is conducted under anhydrous conditions while agitating the mixture maintained by a cooling bath at a temperature of less than about 35°C, preferably from about 20°C to about 30°C. Polymerization is conducted for a time sufficient to form a polyamic acid having the desired molecular weight, usually a period of from about 2 to about 20 hours. The polyamic acid may then be converted to the polyimide by one of several techniques known in the art, for example, by heating the polyamic acid solution until imidization is substantially complete, or by combining the polyamic acid solution and a dehydrating agent, with or without catalyst, and

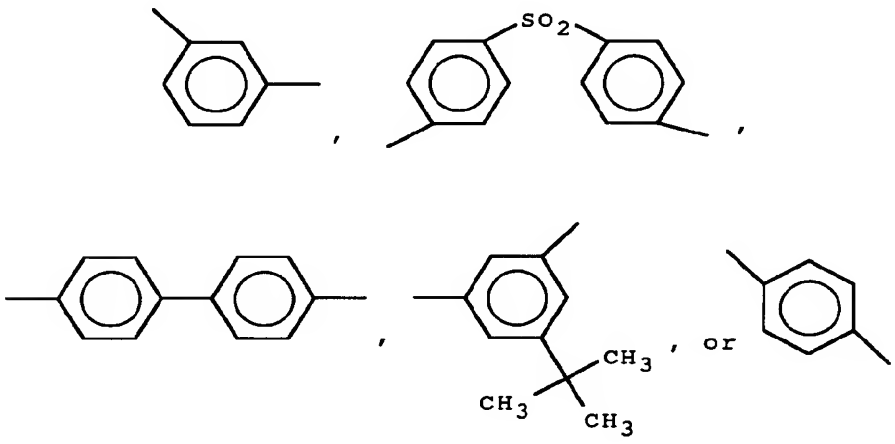
optionally heating the resulting mixture until imidization is complete. The polyimide may then be recovered from solution by precipitation with any suitable non-solvent (e.g., methanol or water) and washed with additional non-solvent.

The resulting polyimides may then, if desired, be blended using conventional solution blending technology to yield a blend having specifically tailored properties.

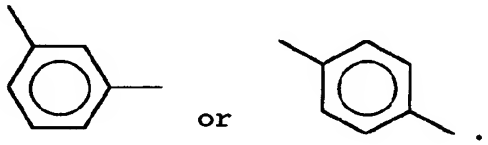
The alkyl-substituted polyamides useful in the present invention contain at least one of the following unit:



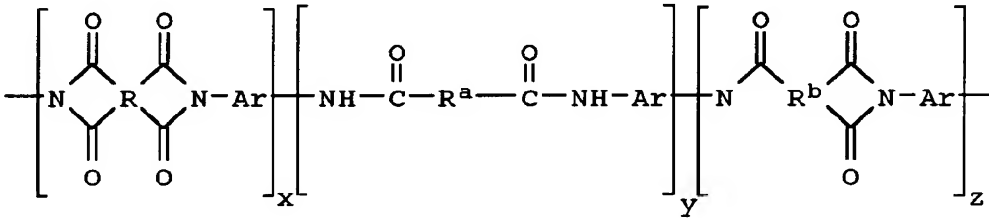
where Ar is defined above and R^a is any aromatic diacid moiety such as



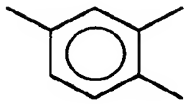
or mixtures thereof, preferably



The alkyl-substituted polyamide-imides useful in the present invention contain at least one of the following unit:



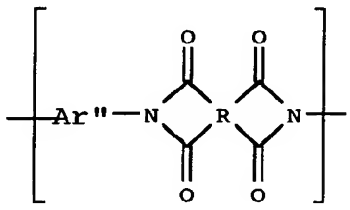
where Ar is defined as above (and may be different in each instance), and R and R^a are as defined above. R^b is any aromatic triacid moeity such as



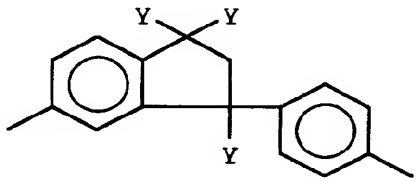
x, y and z are fractions where x + y + z = 1.

The polyamide-imides may also be mixtures of the polyimides and polyamides described above. The polyamides and polyamide-imides may be prepared by methods well known in the art.

An especially useful aromatic polyimide in the present invention has at least one of the following repeating formula:

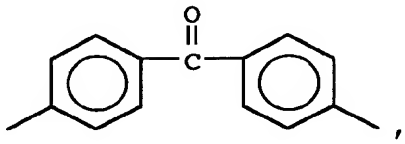


where Ar" is



where R is as defined above and -Y is independently an alkyl group having 1-6 carbon atoms or an aromatic group consisting of 6-12 carbon atoms.

When each -Y is $-CH_3$ and R is



this polymer is commercially available from Ciba-Giegy Company and is generally known as MATRIMID® 5218, which is the preferred composition.

The present invention also provides for gas separation membranes made from a miscible blend of polymers. The polymers employed in the present invention have different molecular structures and different gas permeability and selectivity properties when formed into a membrane, which, when blended, provide a membrane with surprising and superior gas permeability and selectivity.

In particular, the present invention involves a gas separation membrane made from a blend of (i) the aromatic polyethersulfone and the aromatic polyimide, or (ii) the aromatic polyethersulfone, the aromatic polyimide and the alkyl-substituted aromatic polyimide, polyamide or polyamide-imide or mixtures thereof.

As previously indicated, the aromatic polyethersulfone is not generally miscible with the alkyl-substituted polyimides, polyamides or polyamide-imides described herein.

The blended polymers may be mixed in any ratio to achieve the desired properties of the membrane, preferably up to 50% polyethersulfone and up to 50% aromatic polyimide. Not only do the membranes made from the blends achieve surprising and superior gas transport properties, the productivity and selectivity may be conveniently engineered to achieve the desired final properties of the blended polymer membrane.

As previously indicated, the preferred polymers utilized in the present invention are miscible with one an-

other at blend ratios of interest for superior membranes, as evidenced by a single composition dependent glass transition temperature (T_g°C) which is between the highest and lowest glass transition temperatures attributable to respective individual polymer components employed in the blend. To the extent that the polymers are not fully miscible with one another, the resultant membrane will not be uniform and the gas transport properties will, in most cases, be adversely effected. In addition, after annealing the blend above the apparent phase boundary temperature which is above the T_g for the blend, some of the blends may exhibit an irreversible phase separation as evidenced by the presence of two T_g's. This implies that the phase boundary does not represent a true state of equilibrium.

To prepare membranes in accordance with this invention, the resulting blend solution is cast as a sheet onto a support, or spun through a spinneret to yield a hollow fiber. The solvent is then removed. For example, if a uniform membrane is desired, the solvent is evaporated by heating. On the other hand, if an asymmetric membrane is desired, the film or fiber structure is quenched in a liquid which is a nonsolvent for the polymer and a solvent for the organic solvent already present.

As used herein and in the accompanying claims (and as will be appreciated by one of ordinary skill in the art), the term "membrane" or "membranous structure" refers, without limitation, to structures used in separation applications, for example, thin films, thick films, composite structures, asymmetric structures, hollow fibers, modules, and like items.

Membranes are used in the separation of H_2 from other gasses including N_2, CO and CH_4; the separation of CO_2, H_2S and water vapor from natural gas; and the enrichment of air by nitrogen or oxygen. In addition, hydrogen is recovered from ammonia production plants, and, likewise, hydrogen is recovered from coal gasification processes for the production of synthetic fuel.

The standard unit for measuring the permeability of gases through a dense film membrane is the Barrer, which is defined as follows:

$$1 \text{ Barrer} = \frac{10^{-10} \text{ cm}^3 \text{ (STP) x cm.}}{\text{cm}^2 \text{ x sec. x cm. Hg.}}$$

wherein the flux (flow rate) in units of cm^3/sec, being volume per seconds of permeated gas at standard temperature and pressure,

cm. is the thickness of the film,

cm^2 is the area of film, and

cm. Hg is the pressure (or driving force).

The selectivity of a membrane in separating a two-component fluid mixture is defined as the ratio of the rate of passage of the more readily passed component to the rate of passage of the less readily passed component. Selectivity may be obtained directly by contacting a membrane with a known mixture of gasses and analyzing the permeate. Alternatively, a first approximation of the selectivity is obtained by calculating the ratio of the rates of passage of the two components determined separately on the same membrane. Rates of passage may be expressed in Barrer (B) units. As an example of selectivity, $\alpha\ O_2/N_2 = 10$ indicates that the subject membrane allows oxygen gas to pass through at a rate ten times that of nitrogen.

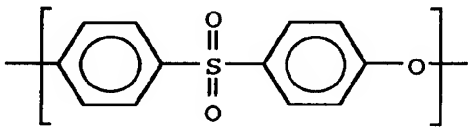
The productivity of an asymmetric membrane is measured in GPUs which is defined as follows:

$$\text{GPU} = 10^{-6} \text{ x } \frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^2 - \text{sec (cm. Hg)}}$$

EXAMPLES

The following examples are illustrative of the polyimide blends and membranes made in accordance with the present invention. The components used in these Examples are as follows:

(1) "Polyethersulfone" or "PES" means VICTREX®, an aromatic polyethersulfone having the following repeating chemical structure:

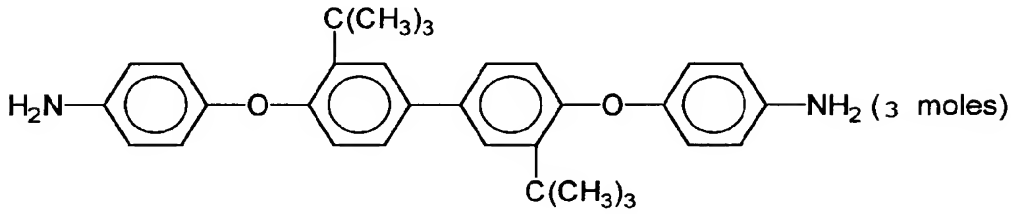


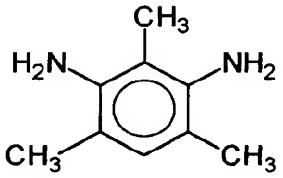
,

which is commercially available from ICI Americas Corporation.

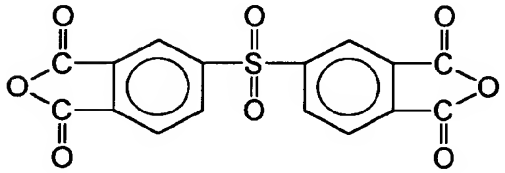
(2) "Aromatic polyimide" means MATRIMID® 5218 which is the polyimide which is the condensation product of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 5(6)-amino-1-(4'-aminophenyl)-1,3,3'-tri-

methylindane commercially available from Ciba-Giegy Corporation.
(3) "Alkyl substituted aromatic polyimide" means a copolyimide formed from:



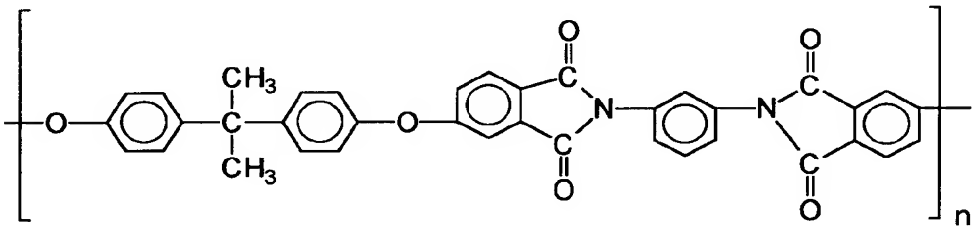


(1 mole) and



(4 moles)

(4) "SYLGARD®" is SYLGARD® 184, an elastomeric silicone material commercially available from Dow Corning Corporation.
(5) "ULTEM®" is ULTEM® 1000 a polyetherimide having the following repeating formula:



commercially available from General Electric Company.

Example 1

This example describes the process for making 50:50 wt. Polyethersulfone ("PES"): aromatic polyimide binary blend dense film samples and for blend miscibility determination and the measurement of the intrinsic O_2/N_2 permeation properties. A 20% wt. solution of 50:50 wt. PES:aromatic polyimide blend solution in N-methylpyrrolidone solvent was prepared. The blend polymer solution was cast on a hot plate maintained at 100°C with a 15 mil (3.84×10^{-5} meter) casting knife gap. After drying on the plate at 100°C for 0.5 hours, the films were further dried in a vacuum oven (20 inches mercury) at room temperature overnight. The films were stripped off the plate and dried in a vacuum oven (20 inches mercury) at 120°C for 4 hours. Five film samples having a thickness range of 1.8 to 2 mils prepared as described above, were tested for mixed gas O_2/N_2 (21/79 mole ratio) permeabilities at 30°C. The average of the permeability and selectivity measurements were:

O_2 Productivity = 1.12 Barrers
O_2/N_2 Selectivity = 6.4

The blend miscibility of the 50:50 wt. PES:aromatic polyimide blend was confirmed by differential scanning calorimetry (DSC). The first heat DSC scan revealed the presence of a single T_g of about 260°C which is in between the T_g's of the individual blend components (Polyethersulfone T_g = 230°C and aromatic polyimide T_g = 318°C). However, following annealing above the T_g of the blend, a second DSC scan revealed the presence of two T_g's corresponding to the individual blend components.

Example 2

This example describes the process for preparing 50:50 wt. PES:aromatic polyimide blend hollow fiber membranes. A polymer solution was prepared with a polymer content of 30% wt. containing 50:50 wt. PES:aromatic polyimide blend polymer and 10.5 wt. % tetramethylenesulfone and 1.8 wt. % acetic anhydride in N-methylpyrrolidone. The above polymer solution was extruded through a hollow fiber spinneret with fiber channel dimensions of outer diameter (OD) equal to 21 mils (533 microns) and inner diameter (ID) equal to 10 mils (254 microns) at the rate of 160 cm^3/hr at 70°C. A solution of 80 volume % N-methylpyrrolidone in water was injected into the bore of the fiber at a rate of 48 cm^3/hr. The spun fiber passed through an air-gap length of 2.5 cm at room temperature into a water coagulant bath maintained at 6°C. The fiber was wound up on a drum at the rate of 100 meters per minute. The water-wet fiber was dehydrated as taught in U.S. Patent No. 4,080,743. This involved the sequential replacement of water with methanol, the replacement of methanol with hexane, followed by drying. The fibers were potted in an epoxy resin at both ends inside a straight steel tubing to provide gas feed through the bore of the fibers. The fibers were tested for mixed gas O_2/N_2 (21/79) with 100 psig bore feed pressure at 21°C. The fibers exhibited the following gas separation properties while producing an inerts enriched product stream containing 95% N_2:

O_2 Productivity = 127 GPU

O_2/N_2 Selectivity = 1.5

The fibers were treated to seal defects protruding through the dense outer gas separating layer as taught in U.S. Patent No. 4,230,463. This involved contacting the outer surface of the fibers with a hexane solution containing 1 % wt. SYLGARD® for a period of 30 minutes at room temperature and at a vacuum of 20 inches mercury in the fiber bore. The hexane was drained and the hollow fibers were allowed to air-dry. The above treated fibers were tested for mixed gas O_2/N_2 (21/79) at 100 psig bore feed pressure and 21°C. The fibers exhibited the following separation performance while producing 95 % N_2:

O_2 Productivity = 16 GPU

O_2/N_2 Selectivity = 6.7

Example 3

This example describes the process for preparing 25:75 wt. PES:aromatic polyimide hollow fiber membranes. A polymer solution was prepared with a polymer content of 30% wt. containing 25:75 wt. PES:aromatic polyimide blend polymer and 10.5 wt. % tetramethylenesulfone and 1.8 wt. % acetic anhydried in N-methylpyrrolidone. The above polymer solution was extruded through the same hollow fiber spinneret described in Example 2 at a rate of 140 cm^3/hr at 80°C. A solution of 80 volume % N-methylpyrrolidone in water was injected into the bore of the fiber at a rate of 45 cm^3/hr. The spun fiber passed through an air-gap length of 2.5 cm at room temperature into a water coagulant bath maintained at 29°C and the fiber was wound up on a drum at the rate of 100 meters per minute. The water-wet fiber was dehydrated and tested for mixed gas O_2/N_2 with 100 psig bore feed as described in Example 2. The results were:

O_2 Productivity = 62 GPU

O_2/N_2 Selectivity = 2.1

The fibers were posttreated by the same procedure described in Example 2 to obtain the following results:

O_2 Productivity = 11.8 GPU

O_2/N_2 Selectivity = 6.1

Example 4

This example describes the preparation of 75:25 wt. PES:aromatic polyimide hollow fiber membranes. A solution containing 37% of 75:25 wt. PES:aromatic polyimide blend and 12.3 wt. % tetramethylenesulfone and 2.2 wt. % acetic anhydride in N-methylpyrrolidone was extruded through a spinneret having the same fiber channel dimensions described in Example 2 at a rate of 160 cm3/hr at 80°C. A bore fluid containing 80 volume % N-methylpyrrolidone in water was injected at a rate of 52.5 cm^3/hr into the bore of the fiber. The spun fiber passed through an air-gap length of 5 cm at ambient temperature into a water coagulation bath maintained at

7°C and was wound up on a drum at a rate of 100 meters per minute. The water-wet fiber was dehydrated as described in Example 2. Gas separation modules were fabricated by inserting loops of hollow fibers in stainless steel tubing while potting the ends of the fibers in an epoxy resin to provide feed gas inlet, rejected gas outlet and permeate gas outlet. The fibers as described above were tested for mixed gas O_2/N_2 (21/79) permeabilities while applying 100 psig on the shell side of the fibers at room temperature. Results are reported below:

O_2 Productivity = 73 GPU

O_2/N_2 Selectivity = 1.3

The fibers were posttreated as described in Example 2 and retested with shell side feed for mixed gas O_2/N_2. Results are reported below:

O_2 Productivity = 12 GPU

O_2/N_2 Selectivity = 6.9

Examples 5-16

These examples describe the process for making 50:25:25 wt. PES:aromatic polyimide: Alkyl-substituted aromatic polyimide ternary blend dense film samples for blend miscibility determination, measurement of the intrinsic mechanical properties and the O_2/N_2 permeation properties. A 20% wt. solution of 50:25:25 wt. PES:aromatic polyimide:Alkyl-substituted aromatic polyimide blend solution in N-methylpyrrolidone was prepared. The solution was cast to obtain dense film samples and tested by the same procedures employed in Example 1. The results of the permeability and selectivity measurements are reported below:

O_2 Productivity = 1.16 Barrers

O_2/N_2 Selectivity = 6.4

The blend miscibility of the 50:25:25 wt. PES:aromatic polyimide: alkyl substituted aromatic polyimide blend was confirmed by DSC. The first heat DSC scan revealed the presence of a single T_g of about 241°C. However, a second heat DSC scan revealed phase separation of the initially miscible blend due to annealing above the T_g of the blend.

The intrinsic O_2/N_2 permeation properties of various PES:aromatic polyimide:alkyl substituted aromatic polyimide ternary blend film samples were tested by the method described in Example 1. The results are report in Table 1.

The intrinsic mechanical properties of various PES:aromatic polyimide:alkyl substituted aromatic polyimide ternary blend film sample were measured. The initial elastic modulus, yield stress and % elongation at break were measured in extension at 23°C according to ASTM D-882 (Tensile Properties of Thin Plastic Sheeting). The results are reported in Table 2.

Table 1

GAS SEPARATION PROPERTIES OF TERNARY BLENDS					
	Composition (Wt. Percent)				
Example	PES	Aromatic Polyimide	Alkyl Substituted Aromatic Polyimide	O_2 Permeability (Barrers)	O_2/N_2 Selectivity
6	80	10	10	1.03	5.62
				1.08	5.57
7	45	45	10	1.31	5.96
				1.31	5.77
8	10	80	10	2.10	5.92
				2.04	6.40
9	10	45	45	2.49	6.10
10	10	10	80	2.74	6.11
11	50	25	25	1.16	6.33
				1.26	6.12
12	40	40	20	1.41	6.39
				1.44	6.12
13	25	50	25	1.60	6.04
14	100	-	-	.75	6.1
15	-	100	-	2.00	7.2
16	-	-	100	4.10	6.25

Table 2

MECHANICAL PROPERTIES OF TERNARY BLENDS						
	Composition (Wt. Percent)					
Example	PES	Aromatic Polyimide	Alkyl Substituted Aromatic Polyimide	E (KSI) Elastic Modulus	Yield Stress (KSI)	Elongation (%)
6	80	10	10	291	11.3	5.4
7	45	45	10	314	12.9	6.5
8	10	80	10	327	14.7	8.2
9	10	45	45	322	14.1	8.8
10	10	10	80	322	10.7	9.6
11	50	25	25	320	14.5	7.6
12	40	40	20	328	12.0	5.2
13	25	50	25	326	13.3	9.9
14	100	-	-	294	7.6	3.3
15	-	100	-	339	13.6	6.6
16	-	-	100	329	14.6	8.4

Example 17

This example describes the process for making 50:25:25 wt PES:aromatic polyimide:Alkyl-substituted aromatic polyimide ternary blend hollow-fiber membranes. A polymer solution was prepared with a polymer content of 30% wt containing 50:25:25 wt PES aromatic polyimide alkyl-substituted aromatic polyimide and 10.5 wt. % tetramethylenesulfone plus 1.8 wt. % acetic anhydride in N-methylpyrrolidone. This polymer solution was extruded through a hollow-fiber spinneret with the same fiber channel dimensions (OD) as described in Example 2 at a rate of 160 cm^3/hr at 70°C. A solution of 80 volume % N-methylpyrrolidone in water was injected into the bore of the fiber at the rate of 48 cm^3/hr. The spun fiber traveled through an air-gap length of 2.5 cm at room temperature into a water coagulant bath maintained at 6°C and the fiber was wound up on a drum at the speed of 100 meters/minute. The fibers were dehydrated and potted in an epoxy resin to provide gas feed through the bore of the fibers as described in Example 2. The fibers were tested for mixed gas O_2/N_2 (21/79) with 100 psig bore feed at room temperature. The fibers exhibited the following separation performance while producing an inert product stream containing 95% N_2:

O_2 Productivity = 121 GPU

O_2/N_2 Selectivity = 2.1

The fibers were posttreated and tested as described in Example 2. The fibers exhibited the following separation performance while producing 95% N_2:

O_2 Productivity = 17 GPU

O_2/N_2 Selectivity = 5.9

The separation performance of the above-treated fibers for other gases were also tested at 100 psig tube-side feed pressure and at room temperature. The single gas permeability data are reported below:

H_2 Productivity = 245 GPU

He Productivity = 242 GPU

N_2 Productivity = 2.3 GPU

CH_4 Productivity = 2.3 GPU

H_2/CH_4 (Single Gas) Selectivity = 107

Example 18

This example describes the process for producing a composite hollow-fiber gas separation membrane comprising a 50:25:25 wt PES:aromatic polyimide:Alkyl-substituted aromatic polymer ternary blend as the separating membrane on a polyimide blend substrate. The substrate polymer is a 90:10 wt ULTEM® and aromatic polyimide.

A substrate solution containing 90:10 weight blend ratio of Ultem:aromatic polyimide is prepared according to the formulation: 31% wt blend polymer and 2.3 wt. % $LiNO_3$ + 9.3 wt. % tetramethylene sulfone and 1.5 wt. % acetic anhydride and 0.3 wt. % acetic acid in N-methylpyrrolidone. The 50:25:25 wt PES:aromatic polyimide:Alkyl-substituted aromatic polyimide ternary blend polymer solution described in Example 17 was used as the separating polymer solution. The above solutions were coextruded through a composite fiber spinneret as described in U.S. Patent No. 5,085,676. The separating layer solution is extruded at a rate of 15 cm^3/hr and the substrate solution is extruded at 125 cm^3/hr. A solution of 90 volume % N-methylpyrrolidone in water is injected to the bore of the fiber at a rate of 48 cm^3/hr while the spinneret is maintained at 90°C. The spun bicomponent fiber is passed through an air-gap of 1 cm at room temperature into a water coagulant bath at 9°C. The composite fiber is wound on a drum at 80 meters/min. The composite fiber is washed and dehydrated by the solvent exchange method as described in Example 2. The fibers were potted at both ends to provide gas feed through the bore of the fibers as described in Example 2. The fibers were tested for mixed gas O_2/N_2 (21/79) with 100 psig bore feed at room temperature. The fibers exhibited the following separation performance while producing an inert enriched product stream containing 95 % N_2:

O_2 Productivity = 49 GPU

O_2/N_2 Selectivity = 2.5

The fibers were posttreated and tested as described in Example 2. The treated composite fibers exhibited the following separation performance while producing 95% N_2:

O_2 Productivity = 16.5 GPU

O_2/N_2 Selectivity = 6.0

Example 19

This example describes the preparation of 10:10:80 wt PES:aromatic polyimide:alkyl-substituted aromatic polyimide ternary blend hollow- fiber membranes. A 28 wt. % polymer solution containing 10:10:80 wt PES:aromatic polyimide:alkyl-substituted aromatic polyimide blend polymer and 9.8 wt. % tetramethylenesulfone and 1.7 wt. % acetic anhydride was extruded through a hollow-fiber spinneret having the same fiber channel dimensions as described in Example 2 at the rate of 120 cm^3/hr and 80°C. A solution of 80 volume % N-methylpyrrolidone in H_2O was injected into the bore of the fiber at the rate of 48 cm^3/hr. The nascent fiber passed through an air-gap length of 7.5 cm at room temperature into a water coagulation bath maintained at 22°C.

The fiber was wound on a drum at the speed of 100 meters/min. The fibers were washed and dehydrated by the same procedure as described in Example 2. Gas separation modules were prepared by inserting loops of the hollow fibers in stainless steel tubing while potting the open ends of the fibers in an epoxy resin to provide feed gas inlet, rejected gas outlet and permeate gas outlet.

The fibers prepared as described above were tested for mixed gas O_2/N_2 (21/79 mole) permeabilities while applying 100 psig on the shell side of the fibers at room temperature. Results are reported below:

O_2 Productivity = 35 GPU

O_2/N_2 Selectivity = 4.2

The fibers were posttreated and tested as described in Example 2. Results are reported below:

O_2 Productivity = 17 GPU

O_2/N_2 Selectivity = 5.6

Example 20

This example describes the preparation of 1:1:1 wt PES:aromatic polyimide:alkyl-substituted aromatic polyimide blend hollow-fiber membranes. A polymer solution containing 30% of the 1:1:1 wt PES:aromatic polyimide:alkyl-substituted aromatic polyimide blend and 9 wt. % tetramethylenesulfone and 1.8 wt. % acetic anhydride was extruded through the same hollow-fiber spinneret described in Example 2 at the rate of 150 cm^3/hr at 71°C. A solution of 80% volume N-methylpyrrolidone in H_2O was injected into the bore of the hollow fiber at the rate of 48 cm^3/hr. The nascent hollow fiber passed through an air-gap length of 5 cm at room temperature into a water coagulation bath maintained at 13°C. The fiber was wound up at the rate of 100 meters/min. The fibers were washed and dehydrated as described in Example 2. Permeators were prepared for testing the

above-prepared hollow fibers as described in Example 19. The fibers were tested for mixed gas O_2/N_2 permeabilities while applying 100 psig shell-side feed pressure at room temperature to obtain the following results:

O_2 Productivity = 26 GPU

O_2/N_2 Selectivity = 3.7

The fibers were posttreated and tested as described in Example 2. The results are reported below:

O_2 Productivity = 12 GPU

O_2/N_2 Selectivity = 6.0

Example 21

This example describes the preparation of 80:10:10 wt PES:aromatic polyimide:alkyl-substituted aromatic polyimide blend hollow fibers. A polymer solution containing 37.5% 80:10:10 wt PES:aromatic polyimide:alkyl-substituted aromatic polyimide and 13.1 wt. % tetramethylenesulfone and 1.5 wt. % acetic anhydride in N-methylpyrrolidone was extruded through the same hollow-fiber spinneret as described in Example 2 at the rate of 150 cm^3/hr at 70°C. A solution of 80% by volume N-methylpyrrolidone in H_2O was injected into the bore of the fiber at the rate of 48 cm^3/hr. The nascent fiber passed through an air-gap length of 5 cm at room temperature into a water coagulation bath maintained at 6°C. The fiber was wound up on a drum at the speed of 100 meters/min.

The fibers were washed, dehydrated and potted in an epoxy resin to fabricate permeators as described in Example 20. The fibers were tested for mixed gas O_2/N_2 at 100 psig shell-side feed pressure and room temperature. The results are reported below:

O_2 Productivity = 16 GPU

O_2/N_2 Selectivity = 1.6

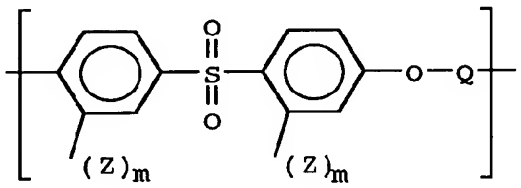
The fibers were posttreated and tested as described in Example 2. The results are reported below:

O_2 Productivity = 8 GPU

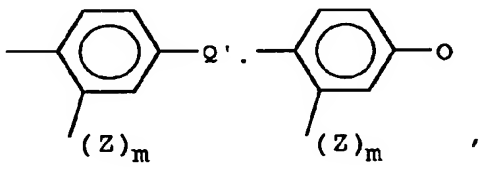
O_2/N_2 Selectivity = 4.7.

Claims

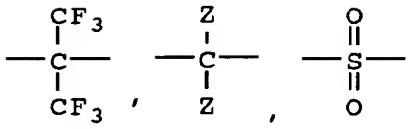
1. A blend comprising (a) an aromatic polyethersulfone, (b) an aromatic polyimide, and (c) an alkyl-substituted aromatic polyimide, polyamide or polyamide-imide or mixtures thereof; wherein the aromatic polyethersulfone contains at least one of the following unit:

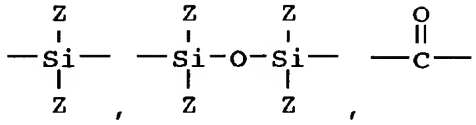


where Q is nothing or has the following formula:

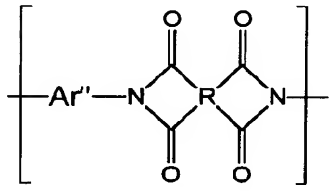


where t is 0 or 1 and Q' is

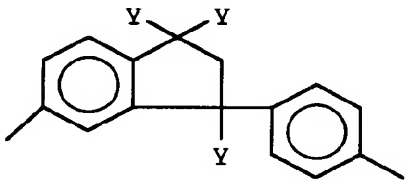




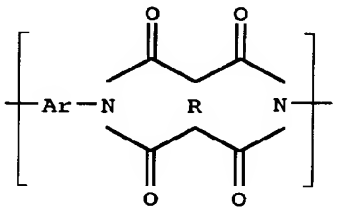
or mixtures thereof;
Z in all cases is independently -H, alkyl groups having 1-6 carbon atoms, aromatic groups having 6-12 carbon atoms, or halogen groups such as -F, -Cl, -Br or -I. Z is preferably -H. m is an integer from 0 to 4; the aromatic polyimide contains at least one of the following unit:



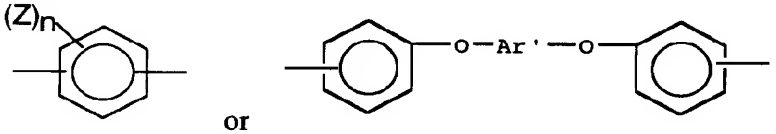
where Ar'' is

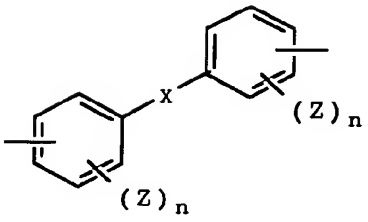


and R is as defined below and Y is an alkyl group having 1-6 carbon atoms or an aromatic group having 6-12 carbon atoms; the alkyl-substituted aromatic polyimide contains at least one of the following unit:

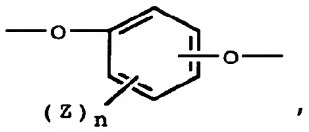


where -Ar- is an aromatic diamine moiety having the following formula:

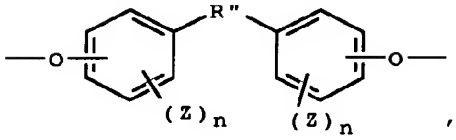


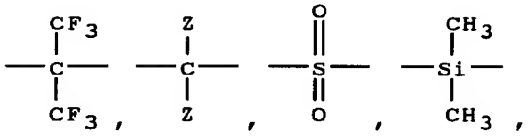


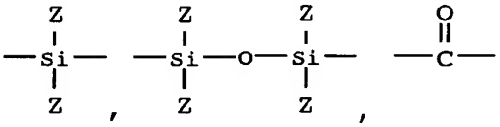
where -Ar'- is
where X = nothing or R';



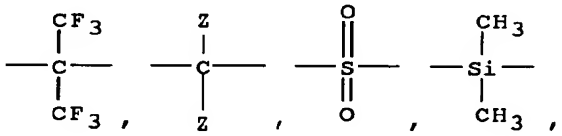
-R'- is

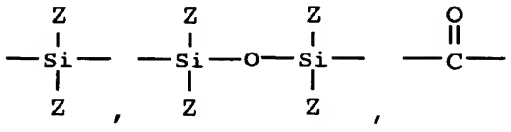




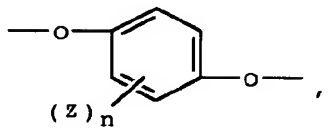


or mixtures thereof, where Z is independently -H, alkyl groups having 1 to 6 carbon atoms, aromatic groups having 6 to 12 carbon atoms, or halogen groups such as -F, -Cl, -Br, or -I, where n is an integer from 0 to 4; R'' is

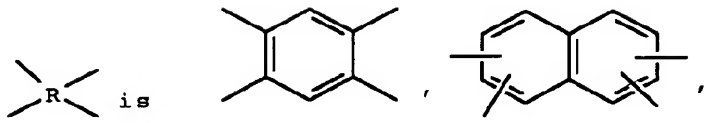


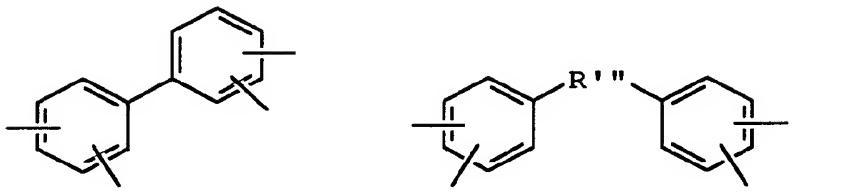


or

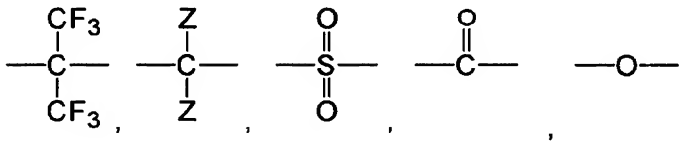


, or mixtures thereof; and

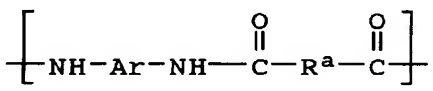




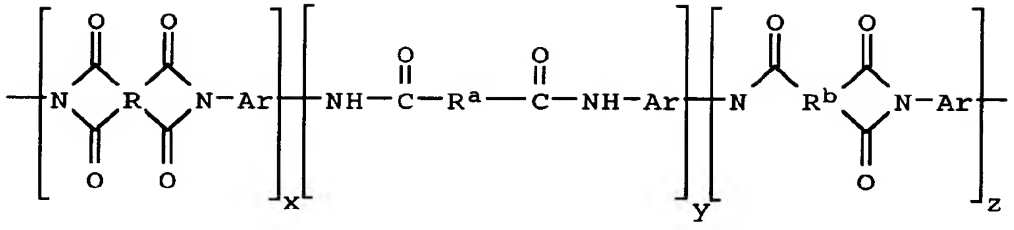
or mixtures thereof;



where R''' is
R' or mixtures thereof; the alkyl-substituted aromatic polyamide contains at least one of the following unit:



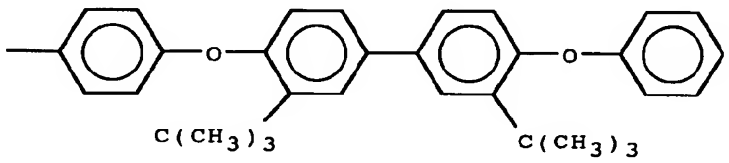
where Ar is defined above and R^a is any aromatic diacid moiety; and the alkyl-substituted aromatic polyamide-imide contains the following unit:



where Ar independently, R and R^a are as defined above, R^b is any aromatic moeity and x, y and z are fractions where x + y + z = 1; or the alkyl-substituted aromatic polyamide-imide materials may also be mixtures of the alkyl-substituted aromatic polyimides and alkyl-substituted aromatic polyamides described above.

2. The blend of claim 1 wherein the blend contains an alkyl-substituted aromatic polyimide and Z is a tertiary butyl group.

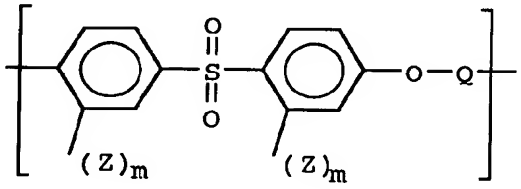
3. The blend of claim 2 wherein Ar is:



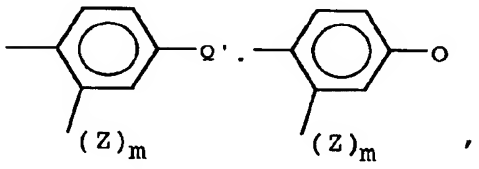
4. The blend according to one of claims 1 to 3 wherein the aromatic polyimide is MATRIMID® 5218.

5. The blend according to one of claims 1 to 4 wherein the aromatic polyethersulfone is VICTREX®.

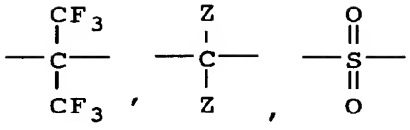
6. A membranous structure for gas separation comprising a miscible blend of (a) an aromatic polyethersulfone and (b) an aromatic polyimide; wherein the aromatic polyethersulfone contains at least one of the following unit:

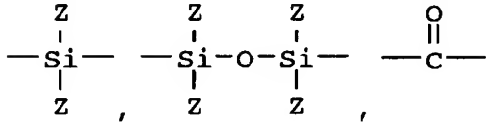


where Q is nothing or has the following formula:

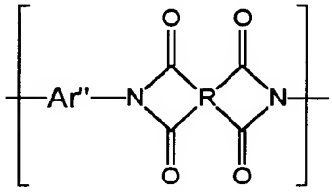


where t is 0 or 1 and Q' is

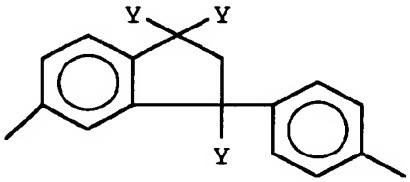




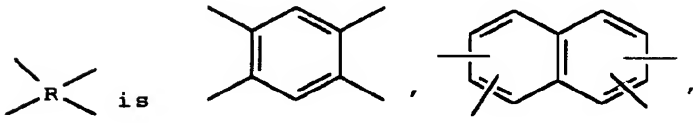
or mixtures thereof;
Z in all cases is independently -H, alkyl groups having 1-6 carbon atoms, aromatic groups having 6-12 carbon atoms, or halogen groups such as -F, -Cl, -Br or -I; m is an integer from 0 to 4; and the aromatic polyimide contains at least one of the following unit:

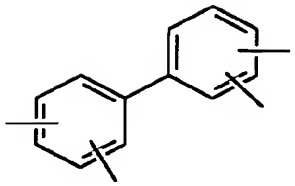
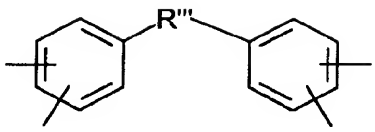


where Ar'' is

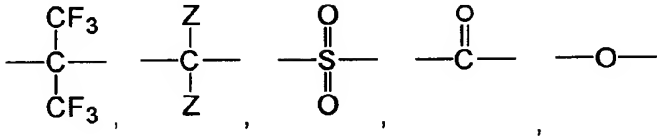


and

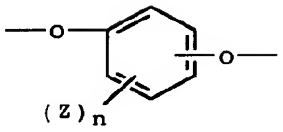



,

,

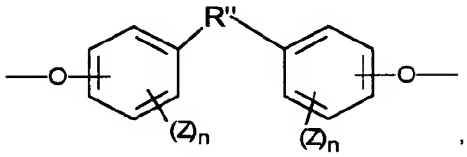
or mixtures thereof,

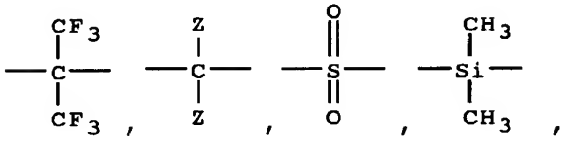


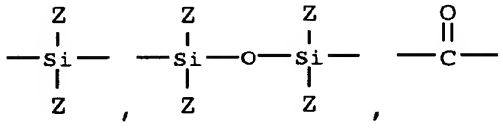
R'''' is
R' described below, or mixtures thereof;


,

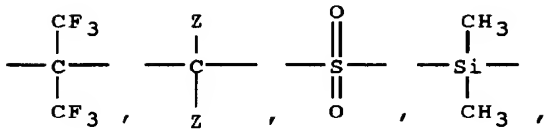
-R'- is

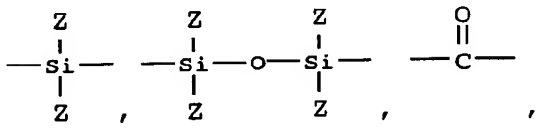

,



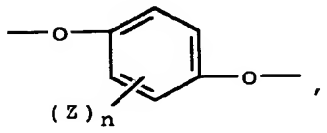


or mixtures thereof, where Z is defined above; R'' is





or

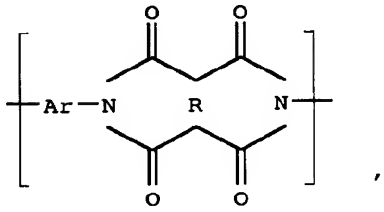


, or mixtures thereof;
and Y is an alkyl group having 1-6 carbon atoms or an aromatic group having 6-12 carbon atoms.

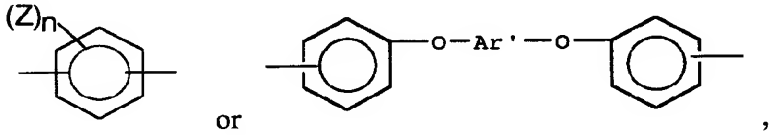
7. The structure of claim 6 wherein the aromatic polyethersulfone is VICTREX®.

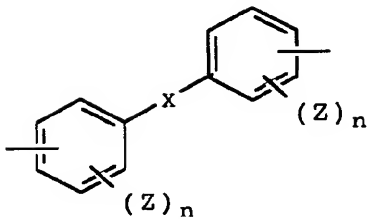
8. The structure according to one of claims 6 or 7 wherein the aromatic polyimide is MATRIMID® 5218.

9. The structure according to one of claims 6 to 8 further comprising a miscible blend of the composition of claim 6 and an alkyl-substituted polyimide, polyamide or polyamide-imide wherein the alkyl-substituted aromatic polyimide contains at least one of the following unit:

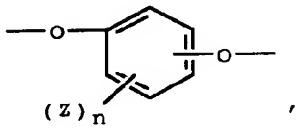


where -Ar- is an aromatic diamine moiety having the following formula:

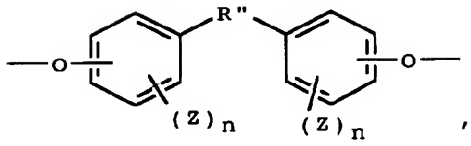


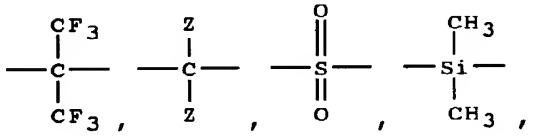


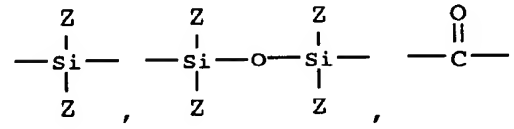
where -Ar'- is
where X = nothing or R';



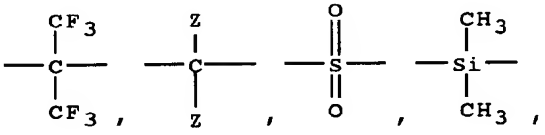
-R'- is

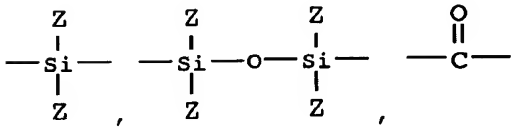




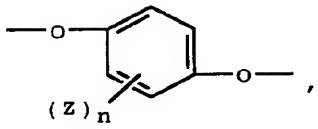


or mixtures thereof, where Z is independently -H, alkyl groups having 1 to 6 carbon atoms, aromatic groups having 6 to 12 carbon atoms, or halogen groups such as -F, -Cl, -Br, or -I, where n is an integer from 0 to 4; R'' is

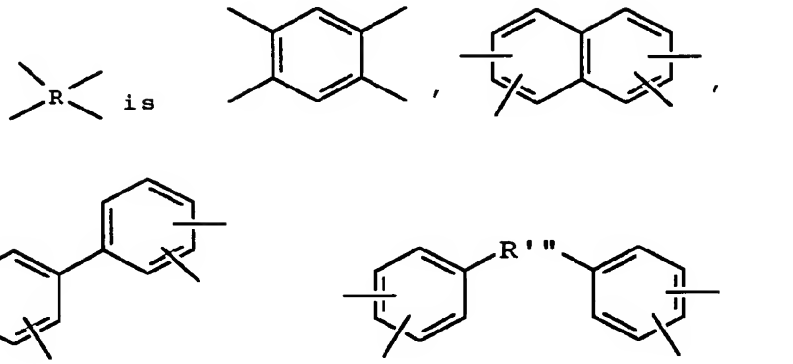




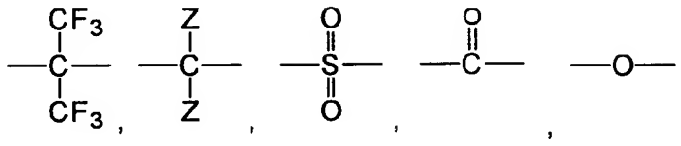
or



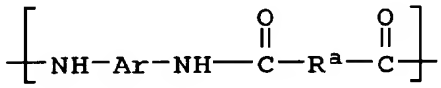
, or mixtures thereof; and



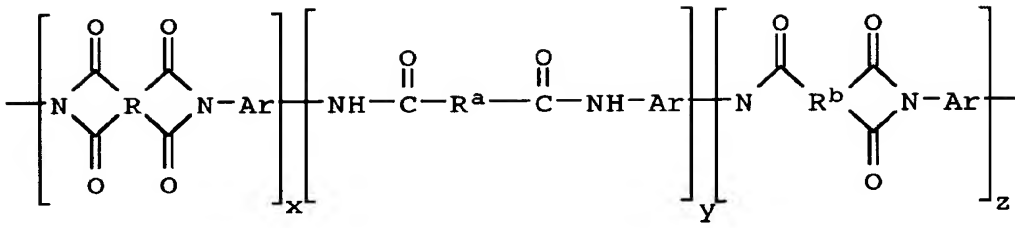
or mixtures thereof;



where R'" is
or R' or mixtures thereof; the alkyl-substituted aromatic polyamide contains at least one of the following unit:



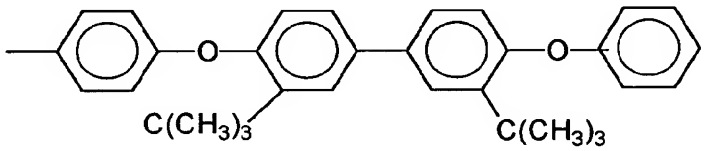
where Ar is defined above and R^a is any aromatic diacid moiety; and the alkyl-substituted aromatic polyamide-imide contains at least one of the the following unit:



where Ar independently, R and R^a are as defined above, R^b is any aromatic moeity and x, y and z are fractions where x + y + z = 1; or the alkyl-substituted aromatic polyamide-imide materials may also be mixtures of the alkyl-substituted aromatic polyimides and alkyl-substituted aromatic polyamides described above.

10. The structure of claim 9 wherein the miscible blend contains an alkyl-substituted aromatic polyimide and Z is a tertiary butyl group.

11. The structure of claim 10 wherein Ar is:



12. The structure according to one of claims 6 to 11 wherein the membrane is an asymmetric membrane or a composite membrane.

13. The structure according to one of claims 6 to 12 wherein the membrane is a hollow fiber membrane.

14. A process for separating one or more gases from a gaseous mixture comprising bringing said gaseous mixture into contact with a first side of a membrane structure according to one of claims 6 to 13 in a manner to cause a portion of the mixture to pass through the membrane to a permeate side, the resulting gas mixture on the permeate side being enriched in one or more component over that of the mixture on the first side.

15. Use of the composition according to one of claims 1 to 5 to manufacture separation membranes, more particularly gas separation membranes.